

# Abstract

Electronic Excitation Energy Transfer is an important intermolecular photophysical process that can affect the excited state lifetime of a chromophore. A molecule in an electronically excited state can return to the ground state by radiative as well as non-radiative processes. During the excited state lifetime, if the chromophore (energy donor) finds a suitable species (energy acceptor) nearby with resonant energy levels, it can transfer the excitation energy to that species and return to the ground state. This process is called Electronic Excitation Energy Transfer. When the energy donor is fluorescent, the process is called Fluorescence Resonance Energy Transfer (FRET) [1]. FRET is a non-radiative process that affects the fluorescence intensity as well as the excited state lifetime of the donor. It occurs due to the electrostatic coulombic interaction between the transition charge densities of the donor and the acceptor. The rate of energy transfer can be evaluated using the Fermi golden rule of quantum mechanics [2].

When the donor and the acceptor are separated by distances that are much larger in comparison with the sizes of the donor and the acceptor, the interaction between them can be thought of as that between their transition dipoles. In such a case, the interaction between the donor and the acceptor is dipolar and the rate of energy transfer has an  $R^{-6}$  dependence, where  $R$  is the distance between the donor and the acceptor [3]. This dependence has first been suggested theoretically by Förster in 1947 [4] followed by the experimental verification by Stryer and Haugland [5]. Since then the process has been used as a spectroscopic ruler to study the conformational dynamics of biopolymers like DNA, RNA, proteins etc [6]. A variety of dye molecules have been explored for donors and acceptors in FRET and the range of distances that can be measured using FRET involving dyes is in the range 1 – 10 *nm*.

When the distances between the donor and the acceptor are not much larger in comparison with their sizes, the dipolar approximation to the interaction is not a very good approximation, thereby leading to deviations from the traditional  $R^{-6}$  dependence. Such non- $R^{-6}$  dependencies are found for polymers, quantum wells, quantum wires etc [7–9]. The interest in such dependencies is due to the need for developing nanoscopic rulers

that can measure distances well beyond 10 *nm*. The objective of our work has been to study energy transfer from fluorophores to various kinds of acceptors that have extended charge densities and understand the distance dependence of the rate of energy transfer [10]. We use the Fermi golden rule as the starting point and develop analytical models for evaluating the rate as a function of the distance between the donor and the acceptor. We study the process of energy transfer from fluorescent dye molecules that serve as energy donors to a variety of energy acceptors namely, graphene, doped graphene, single-walled carbon nanotubes and metal nanoparticles. We also study transfer from fluorophores to a semiconducting sheet and a semiconducting tube of electronic charge density.

There have been experimental studies in the literature of the fluorescence quenching of dyes near single-walled carbon nanotubes [11–13]. But, there are no studies of the distance dependence of rate. Single-walled carbon nanotubes can be thought of as rolled up sheets of graphene. However, interestingly, there were no reports of fluorescence quenching by graphene at the time when we thought of this possibility. Therefore, we first study the process of energy transfer from a fluorophore, which is kept at a distance  $z$  above a layer of graphene to the electronic energy levels of graphene. We find that the long range behavior of the rate has an  $z^{-4}$  dependence on the distance [14, 15]. From our study of transfer from pyrene to graphene, we find that fluorescence quenching can be experimentally observed up to a distance of  $\sim 30$  *nm*, which is quite large in comparison with the traditional FRET limit (10 *nm*). Recent experiments that have been performed after our theory was reported have in fact observed the fluorescence quenching of dyes near graphene. Further, the process has been found to be very useful in fabricating devices based on graphene [16], in eliminating fluorescence signals in resonance Raman spectroscopy [17] and in visualizing graphene based sheets using fluorescence quenching microscopy [18]. The process has also been found to be useful in quantitative DNA analysis [19, 20].

We study the transfer of an amount of energy  $\hbar\Omega$  from a dye molecule to doped graphene [21]. We consider the shift of the Fermi level from the K-point into the conduction band of graphene as a result of doping and evaluate the rate of transfer. We find a crossover of the distance dependence of the rate from  $z^{-4}$  to exponential as the Fermi level is increasingly shifted into the conduction band, with the crossover occurring at a shift of the Fermi level by an amount  $\hbar\Omega/2$ .

We study the process of transfer of excitation energy from a fluorophore kept at a distance  $d$  away from the surface of a carbon nanotube to the electronic energy levels of the nanotube. We find both exponential and  $d^{-5}$  behavior of the rate [22]. For the case of metallic nanotubes, when the emission energy of the fluorophore is less than a threshold, the dependence is exponential. Otherwise, it is  $d^{-5}$ . For the case of semiconducting nanotubes, we find that the rate follows an exponential dependence if the amount of energy that is transferred can cause only the excitonic transition of the tube. However, if any other band gap transition is allowed, the rate follows a  $d^{-5}$  dependence. For the case of transfer from pyrene to a (6, 4) nanotube, we find that energy transfer is appreciable up to a distance of  $\sim 17 \text{ nm}$ .

We then study the process of energy transfer from a fluorophore to a semiconducting sheet of electronic charge density [10]. We find that the rate has an  $z^{-4}$  dependence. For the case of transfer to a semiconducting tube, we find that the rate has a  $d^{-5}$  dependence. The dependencies are in agreement with those obtained for graphene and carbon nanotubes respectively. This shows that the asymptotic distance dependencies are a consequence of the dimensionality of the transition charge densities and are robust.

Strouse *et al.* [23, 24] have studied the process of energy transfer from the dye fluorescein to a  $1.4 \text{ nm}$  diameter gold nanoparticle. Double-stranded DNA molecules of various lengths were used to fix the distances between the donor and the acceptor. The rate was found to have a  $d^{-4}$  distance dependence. They refer to this process as Nanoparticle Surface Energy Transfer (NSET) and the range of distances that can be measured using NSET is more than double that of the traditional FRET experiments. However, theoretical studies that consider the transfer to the plasmonic modes of the nanoparticle find a predominant  $R^{-6}$  dependence [25]. We study the process of energy transfer from the dye fluorescein to a  $1.4 \text{ nm}$  diameter gold nanoparticle considering the excitation of plasmons as well as electron-hole pairs of the nanoparticle [26]. We find that the rate follows the usual Förster type  $R^{-6}$  distance dependence at large distances. But, at short distances, there are contributions of the form  $R^{-n}$  with  $n > 6$ . This is due to the quadrupolar and octupolar modes of excitation of the nanoparticle, the rates corresponding to which have  $R^{-8}$  and  $R^{-10}$  dependencies respectively. Recent calculations using DFT also find similar deviations at short distances [27].